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Ca isotope fingerprints of early crust-mantle evolution

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Abstract—The utility of $^{40}Ca/^{44}Ca$ as a tracer of pre-existing crustal contributions in early Archaean cratons has been explored to identify traces of Hadean crust and to assess the style of continental growth. The relatively short half-life of ^{40}K (~1.3 Gy) means that its decay to ^{40}Ca occurs dominantly during early Earth History. If Archaean crust had a significant component derived from a more ancient protolith, as anticipated by "steady state" crustal evolution models, this should be clearly reflected in radiogenic $^{40}Ca/^{44}Ca$ ratios (or positive initial ε_{Ca}) in different Archaean cratons. A high precision thermal ionisation technique has been used to analyse the $^{40}Ca/^{44}Ca$ ratios of plagioclase separates and associated whole rocks in ~3.6 Ga (early Archaean) samples from Zimbabwe and West Greenland. Three out of four tonalite, trondhjemite, granodiorite (TTG) suite samples from Zimbabwe display initial $^{40}Ca/^{44}Ca$ ratios indistinguishable from our measured modern MORB value (i.e., $\varepsilon_{Ca}(3.6) \sim 0$). Greenland samples, however, are very diverse ranging from $\varepsilon_{Ca}(3.7) = 0.1$ in mafic pillow lavas and felsic sheets from the Isua supracrustal belt, up to very radiogenic signatures ($\varepsilon_{Ca}(3.7) = 2.9$) in both mafic rocks of the Akilia association and felsic TTG from the coastal Amîtsoq gneisses.

At face value, these results imply the Zimbabwe crust is juvenile whereas most Greenland samples include an earlier crustal component. Yet the west Greenland craton, as with many Archaean localities, has experienced a complex geological history and the interpretation of age-corrected initial isotope values requires great care. Both felsic and mafic samples from Greenland display $\varepsilon_{Ca}(3.7)$ so radiogenic that they are not readily explained by crustal growth scenarios. The presence of such radiogenic $^{40}Ca/^{44}Ca$ found in low K/Ca plagioclases requires Ca isotope exchange between plagioclase and whole rock during later metamorphic event(s). In addition the unexpectedly radiogenic Ca isotope ratios in some mafic samples reflect anomalous K/Ca ratios as a result of intense K-metasomatism ~3.6 Ga. Thus Ca isotope measurements are not a robust tracer of crustal growth in the presence of intense tectono-metamorphic processes. Coupled with other isotope data, however, the degree of overprint can be estimated and the $^{40}Ca/^{44}Ca$ ratio of a little disturbed sample hints at a small contribution of Hadean protocrust in the coastal part of the Godthåbsfjord area (Southwest Greenland). In the majority of Zimbabwe TTG samples, unradiogenic initial Ca isotope ratios point to very little prior crustal history and minor subsequent disturbance. We thus infer that the modest initial ε_{Nd} ~0.8 of the Zimbabwean samples is representative of the depleted mantle at ~3.6 Ga. Furthermore, Ca isotope systematics provide little support for a "steady state" model of crustal growth. *Copyright © 2005 Elsevier Ltd*

1. INTRODUCTION

There is little knowledge about the first billion years of Earth evolution. The scant record is stored in the oldest continental rocks, which have been the subject of extensive investigation. Evidence for the existence of continental crust up to 4.4 Ga comes from detrital zircons from the Jack Hills and Mount Narryer, Yilgarn Craton, Western Australia (Wilde et al., 2001). However, the quartzites and conglomerates, which host these zircons, are several hundred million years younger. Today, the oldest rocks on Earth are preserved in Northwest Canada and Southwest Greenland. The ages of these provinces are much debated and range from 3.65 to 4.00 Ga (e.g., Moorbath et al., 1986; Bowring et al., 1989; Nutman et al., 1996; Bowring and Williams, 1999). No terrestrial crustal rock nearly as old as detrital zircons has ever been found. Thus, any Hadean (> 4 Ga) crust has presumably been destroyed. This leaves the outstanding problem of recreating the history of earliest crustal growth.

Two contrasting models of crustal growth were developed some 30 years ago and these have been rigorously discussed ever since. A "steady state" model, presented by Armstrong (1968), suggested that a volume of continental crust similar to that today was formed in a "big bang" scenario very early in Earth's history. Recycling in form of subduction was argued to have balanced the new addition of continental crust through time in this uniformitarian approach. On the contrary, Hurley and Rand (1969) suggested that the age distribution obtained by dating rocks from the continents must reflect the growth rate of the continents itself. Paradoxically, much of the subsequent discussion about the magnitude of early crustal formation has revolved around the signatures of early mantle depletion that are a corollary of the Armstrong model (e.g., Bennett et al., 1993; Bowring and Housh, 1995; Blichert-Toft et al., 1999, Bowring and Williams, 1999; Albarède et al., 2000). Information about the pre-history of Archaean cratons themselves would provide important additional information to the debate.

The $^{176}Hf/^{177}Hf$ of individual grains from the oldest known terrestrial zircons as well as of zircons from the oldest rocks

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have been measured by Amelin et al. (1999, 2000). Zircons have extremely low Lu/Hf ratios and therefore measured Hf isotope ratios reflect the initial Hf isotopic composition of the source. However, the inconsistent values of λ^{176}Lu (Scherer et al., 2001; Bizzarro et al., 2003) lead to contradictory interpretation of the data. Application of one half-life (Scherer et al., 2001) suggests reworking of early formed but small crustal protoliths whereas using the other half-life (Bizzarro et al., 2003), the same Hf data indicate that the oldest zircons and oldest rocks on Earth are derived from an already depleted mantle source.

Given the ambiguities of existing tracers we explore the evidence for early crustal growth using a new approach afforded by the K-Ca isotope system. Here, we present the first ^{40}Ca/^{44}Ca isotope data of plagioclase separates from two Archaean provinces in Greenland and Zimbabwe, to identify crustal pre-history of the crust and to try to distinguish between the "steady state" model of Armstrong (1968) and models of continuous crustal growth.

1.1. K-Ca Systematics and Early Crustal Evolution

The ^{40}K-^{40}Ca system provides temporal information on the evolution of *major* constituents of the continental crust. Previously Ca isotopes have been used for age determinations and granite petrogenesis (Marshall and DePaolo, 1982, 1989; Nelson and McCulloch, 1989; Shih et al., 1993, 1994). The radiogenic ^{40}Ca/^{44}Ca ratio, however, is also an excellent tracer of early crustal growth for the following reasons:

- ^{40}K decays with a short half-life (~1.3 Gy) compared to the age of the Earth, resulting in a non-linear growth of ^{40}Ca with time (Fig. 1a). As a consequence, radiogenic ^{40}Ca/^{44}Ca ratios can be generated in much shorter times in Archaean crust than today. A highly elevated K/Ca for a short period in the Archaean can result in extremely radiogenic Ca, unlike a similarly elevated K/Ca for the same period of time late in Earth history (Fig. 1b). The K-Ca system should thus be more sensitive to the contributions of pre-existing crust during Archaean continental crustal growth than some traditional isotope systems, e.g., in the Sm-Nd system daughter accumulation is near constant through Earth history.
- The very low K/Ca ratio of the mantle (< 0.01; Hart and Zindler, 1986) results in its ^{40}Ca/^{44}Ca remaining effectively constant through time. This hence provides a well-defined baseline against which ^{40}Ca in-growth in prior crust can be clearly detected (Fig. 1a) in contrast to the Lu-Hf system (Scherer et al., 2001; Bizzarro et al., 2003).
- K and Ca are strongly fractionated during continental crust formation. Felsic igneous rocks are characterised by K/Ca ratios over an order of magnitude greater than the mantle and so can evolve significantly radiogenic ^{40}Ca/^{44}Ca signatures. Therefore, Hadean prehistory of any Archaean craton can be detected if the felsic rocks yield radiogenic initial ^{40}Ca/^{44}Ca signatures. If most of the continental crust was formed in a very short time early in Earth's history as proposed by Armstrong (1968), Archaean crustal rocks from all cratons of the world should consistently show a picture of elevated Ca isotope composition.

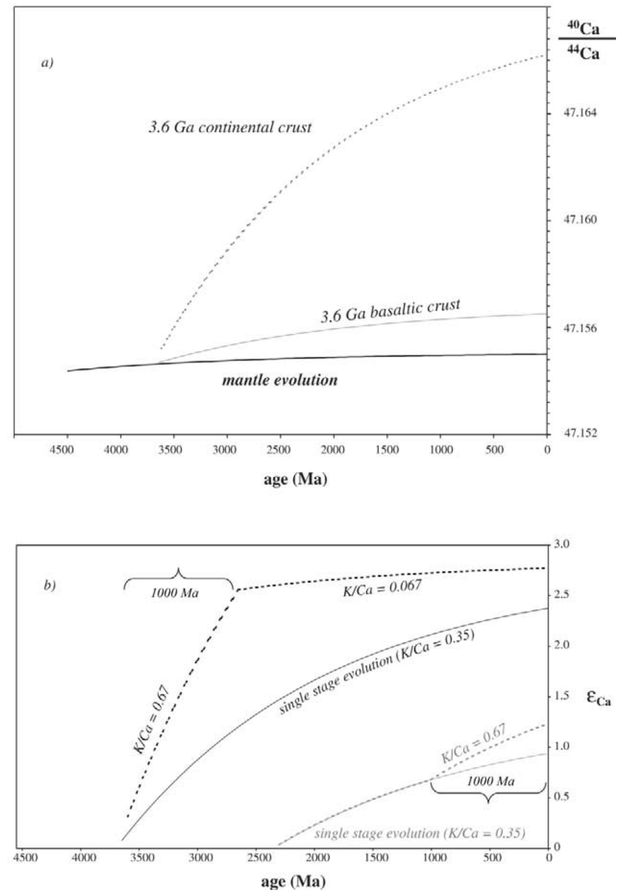


Fig. 1. a: Evolution of the Ca isotopic composition of three different reservoirs with time: mantle with K/Ca of 0.01 (Hart and Zindler, 1986); basaltic crust (K/Ca = 0.05) and continental crust (K/Ca = 0.35; average crustal value taken from Rudnick and Fountain, 1995) formed 3.6 Ga ago. 1b: Four different Ca isotope evolution paths calculated using 50 Ma time intervals. Two continental crustal segments with the same K/Ca ratio of 0.35 but one formed in the Archaean and evolves to 1.5 times greater ε_{Ca} values than the Proterozoic crust. The dashed lines represent two-step crustal evolution paths using two different K/Ca ratios illustrating that a high K/Ca (e.g., K/Ca = 0.67) for a short period (1000 Ma) only during the Archaean results in highly radiogenic Ca.

- Ca is a major constituent in plagioclase minerals, which are also characterised by low K/Ca. Analyses of plagioclase separates should therefore yield the initial ^{40}Ca/^{44}Ca of the sample with minimal age correction. This is a key feature, as the problem of age correction has dogged interpretation of much Archaean isotope data (e.g., Bennett et al., 1993 vs. Gruau et al., 1996; Bowring and Williams, 1999 vs. Moorbath et al., 1997; Kamber and Moorbath, 1998; Blichert-Toft et al., 1999 vs. Villa et al., 2001).

Most Archaean rocks show disturbance and partial resetting of many isotope systems during later tectono-metamorphic events, which indeed can also be a problem for the K-Ca isotope system. Therefore, the measured K/Ca ratio of ancient rocks may not reflect the pristine ratios, resulting in a difficulty of accurate time correction for the ingrown ^{40}Ca from ^{40}K. However, this should not affect the ^{40}Ca/^{44}Ca ratio of most plagioclase measurements, which have low K/Ca and require minor age-correction. Nevertheless, there is the possibility that during metamorphism isotopic re-equilibration occurs and the plagioclase minerals acquires the more radiogenic signature of the host whole rock. Any discrepancy between age-corrected Ca isotopic composition of plagioclase and whole rock, however, will give an indication if the K-Ca system has been disturbed. Elevation of the $^{40}Ca/^{44}Ca$ as a result of regional metamorphic resetting can additionally be tested by measurements of mafic rocks of the same crustal segment. Reworking of pre-existing crust can be invoked to generate radiogenic Ca isotope signatures in felsic but not mafic crust. Assimilation of crustal material from an older protolith can affect the isotope ratios of highly incompatible elements in mafic samples but not major elements such as Ca.

2. SAMPLES

Samples from two early (-mid) Archaean cratons were chosen for analysis. A suite from southern West Greenland comprises three TTG gneisses from the coastal Godthåbsfjord area (Amîtsoq gneisses, part of the Itsaq gneiss complex), two felsic sheets within the pillow sequence as well as two meta-pillow basalts of the Isua supracrustal belt (ISB), and three mafic rocks from the Akilia association (Table 1). Samples from the Zimbabwe Craton consist of four TTG gneisses from the Shabani-Mashaba area (Table 1). Most samples have been previously investigated for geochemistry and several isotope systems (Rb-Sr, Th-U-Pb, Sm-Nd; Re-Os, e.g., Black et al., 1971; Moorbath et al., 1972, 1973, 1975, 1976, 1977a, 1977b, 1986; Baadsgaard, 1973; Hawkesworth et al., 1975; Taylor et al., 1984, 1991; Baadsgaard et al., 1986a, 1986b; Bennett et al., 1993; Luais and Hawkesworth, 1994; Kamber and Moorbath, 1998; Whitehouse et al., 1999; Frei et al., 1999, 2002, 2004; Whitehouse and Kamber, 2002, 2003; Frei and Jensen, 2003).

Whole rock Rb-Sr, Sm-Nd and Pb-Pb analyses all point to an intrusion age of ~3.65 Ga for the Amîtsoq gneisses (Greenland). However, the fact that some of these rocks (e.g., 110999) contain older zircons, up to 3.85 Ga, has led to a continuing debate as to whether these older zircons are inherited or truly reflect the intrusion age (Bennett et al., 1993; Nutman et al., 1996; Kamber and Moorbath, 1998; Whitehouse et al., 1999). The age of the Akilia association is also controversial (3.7 Ga vs. >3.85 Ga; Schiøtte and Compston, 1990; Nutman et al., 1997a; Kamber and Moorbath, 1998; Myers and Crowley, 2000) but the rocks are definitively older than the surrounding Amîtsoq gneisses (McGregor and Mason, 1977). The deposition of the volcanic and chemical-sedimentary rocks of the ISB, on the other hand, is comparatively well defined and took place at 3.71 Ga and at 3.81 Ga for some lithologies (Moorbath et al., 1973; Nutman et al., 1997b; Kamber et al., 1998; Blichert-Toft et al., 1999; Frei et al., 1999; Villa et al., 2001).

A detailed geochronological description of the Zimbabwe Craton has been given by Taylor et al. (1991). The oldest rocks intruded at ~3.6 Ga and are exposed in the Shabani-Mashaba area north of the Belingwe Greenstone Belt (Hawkesworth et al., 1975; Moorbath et al., 1977b). The selected TTG are mostly tonalitic banded gneisses characterised by low Rb concentrations and only slightly evolved Sr isotopic compositions ($^{87}Sr/^{86}Sr_i$ ~ 0.700) as well as ε_{Nd} values of around 0.8 (Moorbath et al., 1976, 1977b).

The Greenland samples underwent widespread early Archaean granulite facies metamorphism around 3.6 Ga and one late Archaean upper amphibolite facies metamorphism approximately at 2.7 Ga (e.g., Black et al., 1971; Pankhurst et al., 1973a; Griffin et al., 1980; Nutman et al., 1996; Whitehouse et al., 1999; Frei et al., 2002). The oldest rocks of the Zimbabwe Craton are affected by several stages of younger intrusions and crustal reworking between 2.8 and 2.6 Ga (Hawkesworth et al. 1975; Moorbath et al., 1977b, 1986; Hickman, 1978).

3. ANALYTICAL METHODS

Whole rock analyses were made on splits of existing powders. Plagioclase separates were prepared by hand picking from a stained, density separated bulk feldspar fraction. Chemical procedures were modified after Nägler and Villa (2000). Subboiled distilled acids were used exclusively. ~0.1 mg of handpicked plagioclase and ≥1.5 mg whole rock powder were digested in a hot $HF-HNO_3$ mixture (4:1) in Savillex screw-top beakers followed by a hot concentrated HCl attack. The chemical separation of Ca was performed using 1 mL teflon columns loaded with cleaned Dowex 50W-8X cation exchange resin. Samples were loaded in 1 mL >8M HBr, and washed with further 4 mL >8M HBr to elute the alkalis, Mg, Mn and Al. Ca is collected in 4 mL 5M HBr and subsequently evaporated. In a second clean-up column Ca is separated from Fe and Ti as well as traces of the other elements (Sr and the HREE) using 5 mL 2M HCl and Ca is finally collected in 3 mL 4M HCl.

Measurement of Ca isotopes poses some significant mass-spectrometric problems: *i)* large dispersion of isotopes of interest, making simultaneous collection difficult (Fletcher et al., 1997a); *ii)* large ratios requiring high dynamic range ($^{40}Ca/^{44}Ca$ ~47, $^{40}Ca/^{42}Ca$ ~151); *iii)* small radiogenic component in overall ^{40}Ca signal requiring accurate measurements to resolve variations. Measurements in this study were made on a ThermoFinnigan Triton, thermal ionisation mass-spectrometer (TIMS), which has specifications well suited to tackling the measurement of Ca isotopes. The 10^{11} ohm feedback amplifiers have a 50V range, allowing the major ^{40}Ca beam to be measured simultaneously with sufficiently intense ^{42}Ca and ^{44}Ca signals. The Triton permits simultaneous measurement of isotopes over a 15% mass dispersion whilst maintaining good peak shapes. Thus all the Ca isotopes of interest could be analysed in a single "static" measurement.

Each sample yielded some 2–20 μg of Ca, which was subsequently dissolved in 2 μL of 0.2M HNO_3 and loaded onto degassed zone refined Re-filaments, as part of a double Re filament assemblage. A stable ion beam was usually reached at a temperature ranging from 1605 to 1630°C, which corresponds to a current of 3.2 to 3.9 A for the ionisation filament. The current of the evaporation filament ranged from 1.4 to 1.8 A. 20 μg Ca yielded a ^{40}Ca signal of ≥20V at this temperature and even the less abundant isotope ^{43}Ca exceeds 30 to 40 mV. Analyses comprise ≥20 blocks of 10 cycles, with an aim of attaining a standard error of better than 0.002%. The settings of the mass spectrometer include integration times of 8.4s, idle times of 3s, 1 min baseline measurements before each block and lens focus every fifth block as well as amplifier rotation (to remove differential electronic gain between Faraday cups). An interference correction for ^{40}K on ^{40}Ca is made measuring ^{41}K and assuming a $^{41}K/^{40}K$ ratio of 575.8, but the magnitude of this correction is generally less than 2 ppm. The measured $^{40}Ca/^{44}Ca$ ratios were corrected for fractionation using the $^{42}Ca/^{44}Ca$ ratio of 0.31221 and an exponential law (Russell et al., 1978; Hart and Zindler, 1989). Typically samples show a smooth variation of $^{42}Ca/^{44}Ca$ during analysis from 0.315–0.313.

During the time of analyses the internal precision was better than 0.5 ε_{Ca} and reproducibility around 1 ε_{Ca} (SRM 915a: 47.1604 ± 0.0043; 92 ppm 2σ stdev., n = 19). However, in a later stage of analysis, samples could be reproduced to <0.5 ε_{Ca} once an optimal experimental procedure has been established and minor changes in chemistry and loading techniques ceased.

The K and Ca contents in plagioclase and whole rocks were mea-

Table 1. Ca isotope data and K/C ratios of TTG gneisses and mafic rocks from Greenland and Zimbabwe

Sample	Rock description^	Locality^	Mineralogy	$^{40}Ca/^{44}Ca$§	±SE*	n	ε_{Ca}°	(0)*	K/Ca**	t(Ga)	$^{40}Ca/^{44}Ca(t)$#	$\varepsilon_{Ca}(t)$#
Greenland TTGs												
125519 Fsp				47.1655	±0.0017	4	2.2	±0.4	0.060	3.65	47.1634	1.8
125519 WR	melanocratic, banded, tonalitic gneiss	near Narssaq	Pl, Qtz, Hbi, Bt, Sph, Ap, ore	47.1696	±0.0009	3	3.1	±0.2	0.935	3.65	47.1376	−3.7
125540 Fsp				47.1795	±0.0027	3	5.2	±0.6	0.540	3.65	47.1610	1.3
125540 WR	leucocratic, homogeneous, granodioritic gneiss	Iviangit	Pl, Qtz, Ktsp, Bt, Ep	47.1880	±0.0022	2	7.0	±0.5	0.964	3.65	47.1550	0.0
110999 Fsp				47.1703	±0.0032	3	3.2	±0.7	0.046	3.65	47.1687	2.9
110999 WR	mesocratic, banded, tonalitic gneiss	E coast of Angissorssuaq	Pl, Qtz, Bt, Hbi, Ep, Sph	47.1781	±0.0028	3	4.9	±0.9	0.190	3.65	47.1716	3.5
460034 Fsp				47.1747	±0.0043	1	4.2	±0.9	0.459	3.71	47.1584	0.7
460034 WR	tonalitic sheet within pillow sequence	western Isua supracrustal belt	Pl, Qtz, Grt, Bt, carbonates and sulfides	47.1829	±0.0043	1	5.9	±0.9	0.769	3.71	47.1556	0.1
460074b Fsp				47.1560	±0.0043	1	0.2	±0.9	0.016	3.71	47.1554	0.1
460074b WR	felsic intrusive sheet of pillow basalt 460074a	western Isua supracrustal belt	Pl, Qtz, Bt	47.1599	±0.0013	2	1.0	±0.3	0.061	3.71	47.1577	0.6
Greenland Mafics												
SM/GR/97/4 Pl				47.1670	±0.0007	4	2.5	±0.1	0.006	3.70	47.1668	2.5
SM/GR/97/4 WR	biotite-amphibolite	Akilla	Hbl, Pt, Bt	47.1674	±0.0027	2	2.6	±0.6	0.384	3.70	47.1538	−0.2
SM/GR/97/12 Pl				47.1669	±0.0031	3	2.5	±0.7	0.003	3.70	47.1668	2.5
SM/GR/97/12 WR	biotite-amphiboitte	Innersuartuut	Hbl, Pt, Bt	47.1634	±0.0043	1	1.8	±0.9	0.266	3.70	47.1540	−0.2
SM/GR/97/17 Pl				47.1627	±0.0015	4	1.6	±0.3	0.005	3.70	47.1625	1.6
SM/GR/97/17 WR	amphibolite	Akilla	Hbl, Pl, Bt	47.1642	±0.0043	1	2.0	±0.9	0.048	3.70	47.1625	1.6
94-66a Pl				47.1603	±0.0043	1	1.1	±0.9	0.084	3.71	47.1573	0.5
94-66a WR	coarse grained meta-pillow basalt	western lsua supracrustal belt	Hbl, Pl, ±Bt, ±Aln	47.1615	±0.0043	1	1.4	±0.9	0.026	3.71	47.1606	1.2
460074a Pl				47.1573	±0.0043	1	0.5	±0.9		3.71		
460074a WR	fine grained meta-pillow basalt (deformed)	western Isua supracrustal belt	Hbl, Pl, Bt. Aln	47.1605	±0.0001	2	1.2	±0.0	0.054	3.71	47.1586	0.8
Zimbabwe TTGs												
ZB89-23 Fsp				47.1627	±0.0016	2	1.6	±0.3	0.173	3.57	47.1571	0.4
ZB89-23 WR	fine grained, foliated tonalitic gneiss	Lundi river	Qtz, ser. Pl, Kfsp, chl. Bt, Cpx, ±Ap, Ep, Sph	47.1742	±0.0017	2	4.1	±0.4	0.487	3.57	47.1584	0.7
ZB89-64 Fsp				47.1657	±0.0011	5	2.3	±0.2	0.082	3.57	47.1630	1.7
ZB89-64 WR	foliated tonalitic gneiss	Ngezi river	Qtz, Pl, Kfsp, Chl, Bt, Zrn, Rt, Ep(Aln), ±Ap, Sph, ore	47.1745	±0.0037	4	4.1	±0.8	0.276	3.57	47.1655	2.2
ZB89-21 Fsp				47.1637	±0.0010	3	1.9	±0.2	0.249	3.57	47.1556	0.1
ZB89-21 WR	strongly banded, tonalitic gneiss	Lundi river	white: Qtz, Kfsp, Pl, ±Bt; dark: Qtz, Fsp, chl. Bt, Ep(Aln), Ms, Sph	47.1657	±0.0030	2	2.3	±0.6	0.657	3.57	47.1444	−2.3
ZB89-17 Fsp				47.1566	±0.0018	3	0.3	±0.4	0.062	3.57	47.1546	−0.1
ZB89-17 WR	strongly banded, granodioritic gneiss	Nyarutedzi river	Qtz. perthitic Orth, Pl. chl. Bt, Ep(Aln), Ap, Cc, Zrn, ores	47.1622	±0.0006	2	1.5	±0.1	0.449	3.57	47.1476	−1.6

^taken from Moorboth et al., (1972); Luais and Hawkesworth (1994) and Frei et al., (2002)
§ =frac. corrected using $^{42}Ca/^{44}Ca = 0.31221$ (Russell et al., 1978)
* = propagated standard error of n replicate measurements, if n = 1: 2σ external reproducibility (standard deviation of SRM 915a)
° = calculated using MORB glass PH78-2 as reference. $^{40}Ca/^{44}Ca = 47.1550 \pm 11$
** = measured using ICP-AES, GeoPT3(YG-1): K = 3.913%, Ca = 0.735%
# = age corrected values
n = number of measurements
fsp = feldspar fraction and stained and picked piagioclase fraction, WR = whole rock

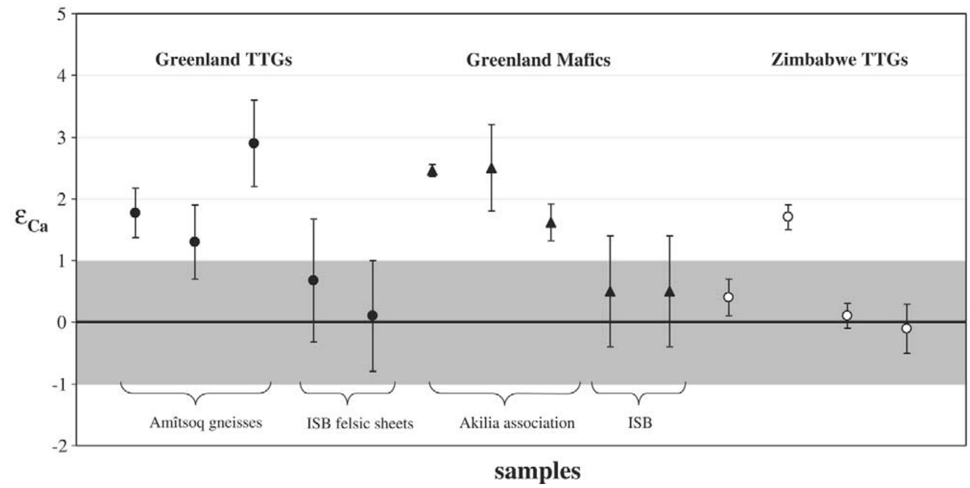


Fig. 2. Age-corrected Ca isotope data of plagioclase separates. Analysed rocks are three coastal Amîtsoq TTG gneisses from the Itsaq Gneiss Complex and two felsic sheets within the Isua supracrustal belt—ISB (circles), three metagabbros from the Akilia association and two metabasalts from the ISB (triangles) sampled in Greenland (filled symbols) as well as four TTG gneisses from the Shabani-Mashaba area in Zimbabwe (open symbols). The error bars reflect 1σ reproducibility of n measurements (Table 1) and the shaded area the 2σ external reproducibility of $1\varepsilon_{Ca}$ around our measured mantle value.

sured by ICP-AES but using different sample splits to those analysed for Ca isotope ratios. The Yewrangara Granite YG-1 (GeoPT3) has been taken as a rock standard and the measured K and Ca concentrations deviate by 7% from the mean of 67 and 65 analyses, respectively (Thompson et al., 1999). However, the K/Ca ratio differs by only 0.2%. The measured K/Ca ratios were used for correction of ingrown ^{40}Ca from ^{40}K.

4. RESULTS

Feldspar and whole rock data are presented in Figures 2, 3 and 4 and Table 1. The measured $^{40}Ca/^{44}Ca$ ratios are expressed as ε_{Ca} [$\varepsilon_{Ca} = \{(^{40}Ca/^{44}Ca)_{sample}/(^{40}Ca/^{44}Ca)_{mantle}-1\}\times 10^4$]. The reference value used for the mantle is a MORB glass measured using the same analytical procedure, $^{40}Ca/^{44}Ca = 47.1550 \pm 0.0011$ (20 ppm 2σ stdev.; $n = 2$) of sample PH78–2 (Niu et al., 1999). As mentioned earlier, ingrowth of ^{40}Ca at the low K/Ca of the mantle over Earth history is small compared to analytical error (Fig. 1a), and so this present day value serves as an appropriate mantle reference for all samples.

Our crustal samples are corrected for the K decay since their formation using the total K decay constant of $\lambda = 0.5543$ Gy^{-1} (Steiger and Jäger, 1977) and the recently determined branching ratio of 0.8933 (Nägler and Villa, 2000). Ages of 3.65 Gy (Kamber and Moorbath, 1998) and 3.57 Gy (Hawkesworth et al., 1975; Moorbath et al., 1977b) were taken for Greenland and Zimbabwe TTG gneisses, respectively. Nevertheless, due to small K/Ca ratios of the plagioclase minerals, an age difference of 150 Ma (e.g., 3.8 Ga as formation age for the Amîtsoq gneisses proposed by Nutman et al., 1996, 1999) would decrease the $^{40}Ca/^{44}Ca$ of the plagioclase separates by less than 0.1 ε_{Ca} (with the exception of sample 125540 which would show a $\Delta\varepsilon_{Ca} = 0.4$, however, this sample yields straightforward ~3.65Ga ion-microprobe zircon ages: Whitehouse et al., 1999). The three mafic rocks from the Akilia association as well as the four samples from the ISB are corrected using the age of 3.7 Ga and 3.71 Ga, respectively (e.g., Nutman et al., 1997b; Kamber and Moorbath, 1998; Frei et al., 1999, 2002).

Age-corrected ε_{Ca} values of the plagioclases of the Zimbabwe TTG gneisses range from -0.1 to 1.7, with three of the four in error of mantle values (Fig. 2). Reassuringly two metabasalts from ISB yield values of $\varepsilon_{Ca} = 0.5$ within error of the mantle. The Ca isotopic composition of the two felsic sheets within the metabasalts from the ISB also yields Ca isotope ratios indistinguishable from the mantle. In contrast, plagioclases from the coastal Amîtsoq gneisses (Greenland) yield radiogenic initial ε_{Ca} with values ranging from 1.3 to 2.9. Furthermore, the mafic samples from the Akilia association (Greenland) have plagioclases with ε_{Ca} (1.6–2.5) as radiogenic as the Amîtsoq gneisses (Fig. 2).

Thus, 3 of 5 analysed plagioclase separates of felsic rocks from Greenland are characterised by radiogenic Ca isotope ratios in contrast to 1 in 4 from the Zimbabwe TTG gneisses. It is notable that some of those plagioclase separates have higher K/Ca than anticipated and so require a larger age correction than is ideal (Table 1). Yet the distinction between mostly radiogenic Greenland plagioclases and Zimbabwean samples with $^{40}Ca/^{44}Ca$ as low as mantle values remains even if only the lowest K/Ca plagioclases are considered. Perhaps the most striking observation, however, is that the mafic samples from the Akilia association (Greenland) also have significantly radiogenic plagioclases.

5. DISCUSSION

Two end member models of bulk crustal Ca isotope evolution, "steady-state" (e.g., Armstrong, 1981; grey line) and continuous growth (e.g., Taylor and McLennan, 1985; black line), are illustrated in Figure 3. The two models predict very different Ca isotopic evolution paths for the continental crust. The age-corrected Ca isotope data of the plagioclase separates from Figure 2 are plotted for comparison. The initial ε_{Ca} values for the majority of our Zimbabwe samples are clearly inconsistent with the "steady state" model. The Greenland case is more

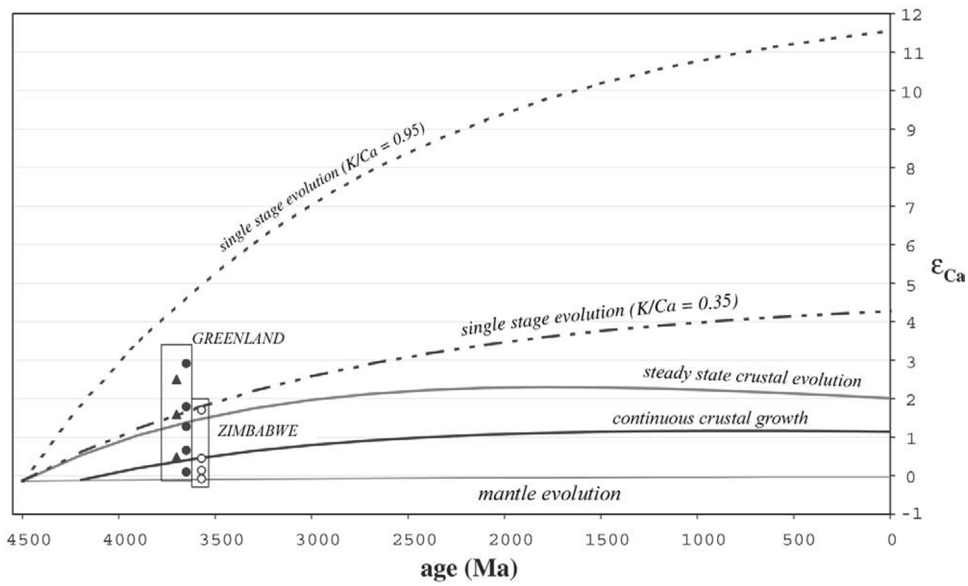


Fig. 3. Ca isotope evolution diagram showing a 15-step modelled steady state crustal evolution allowing crustal recycling into the mantle (grey lines) and a continuous crustal growth. Note the nearly constant mantle curve. Additionally two single stage crustal evolution paths of two 4.5 Ga old crustal segments with different K/Ca are plotted (average crust: K/Ca = 0.35 and upper crust: K/Ca = 0.95; Rudnick and Fountain, 1995) as well as the age-corrected data from Figure 2.

complex. Initial ε_{Ca} in the Greenland plagioclases scatter from mantle values up to values even higher than predicted by a "steady state" model. Indeed the $\varepsilon_{Ca}(t)$ of some Greenland plagioclases are as high or higher than one of the extreme closed system evolution paths of putative crustal segments that have existed since the beginning of Earth History (Fig. 3). As stressed above, a striking and important additional observation is that the *mafic* rocks from the Akilia association show radiogenic Ca signatures comparable to the Amîtsoq TTG gneisses. The Ca isotopic compositions of the mafic Akilia enclaves must have been disturbed to reach such elevated ratios. Likewise the scatter of the other Greenland samples can potentially be attributed to disturbance during later tectono-metamorphic events. Even if some of the radiogenic initial Ca ratios in the Greenland samples were attributable to signs of a component of Hadean crust, the Armstrong model requires large volumes of crustal reworking. Thus radiogenic Ca isotope signature should also be present in the rocks of the Zimbabwe craton, which is not the case for most of the analysed samples. Therefore we find little support for a "steady state" model of crustal evolution in this study.

5.1. Metamorphic Overprint

To investigate further possible disturbance of the K-Ca system, age-corrected ε_{Ca} of plagioclase and corresponding whole rock can be compared (Fig. 4). An undisturbed sample must have concordant age-corrected plagioclase and whole rock $^{40}Ca/^{44}Ca$, although this condition is not sufficient to guarantee closed system behaviour. As can clearly be seen from Figure 4, above all the Amîtsoq gneisses as well as the mafics from the Akilia association (Greenland) show the largest degree of disturbance. The Ca isotope ratios of all the plagioclases from the mafic Akilia enclaves are more radiogenic than mantle values and some substantially so. In these mafic rocks, remobilisation of large proportions of pre-existing silicic crust cannot be invoked to account for such radiogenic values. The samples from the Akilia association thus provide an important indication of how metamorphism can perturb Ca isotope systematics.

To understand the implications of metamorphic disturbance of the Ca isotope system it is necessary to consider the diffusivity of Ca. Shi et al., (1994) pointed out that Ca diffusion in lunar granites is by a factor of ten slower than Sr diffusion. In contrast Fletcher et al., (1997b) report that the diffusion coefficient of Ca in micas is about an order of magnitude higher than that of Sr. Although imperfect, Sr diffusion can be used as an analog for Ca. The diffusion coefficients of Sr are low in plagioclase minerals even at temperatures exceeding 700°C ($<10^{-16}$cm^2/s; Cherniak and Watson, 1994; Giletti and Casserly, 1994). A high temperature thermal event must have lasted for ~300 of million years to reach Sr isotopic equilibrium between plagioclase and whole rock in a coarse grained rock (feldspar crystals ~1 cm^3 in size). Pure Ca diffusion thus seems unlikely to account for the radiogenic signatures in the measured plagioclase minerals.

Recrystallisation of the plagioclase minerals, however, could be a process during which plagioclases exchange their Ca isotopes with surrounding high K/Ca whole rock during later high temperature metamorphism. In Southwest Greenland such an event was last recognised at 2.7 Ga. This in turn implies that the radiogenic Ca isotope signatures documented in the plagioclases of the mafic Akilia enclaves were present at 2.7 Ga (Fig. 5), presumablyas a result of ^{40}Ca ingrowth since extensive K metasomatism at ~3.6 Ga (Rose et al., 1996; Rosing et al., 1996; Frei et al., 1999; Fedo and Whitehouse, 2002). The 2.7 Ga metamorphic event plausibly reduced the K/Ca ratio of the whole rock, due to biotite dehydration, 'freezing' in this radio-

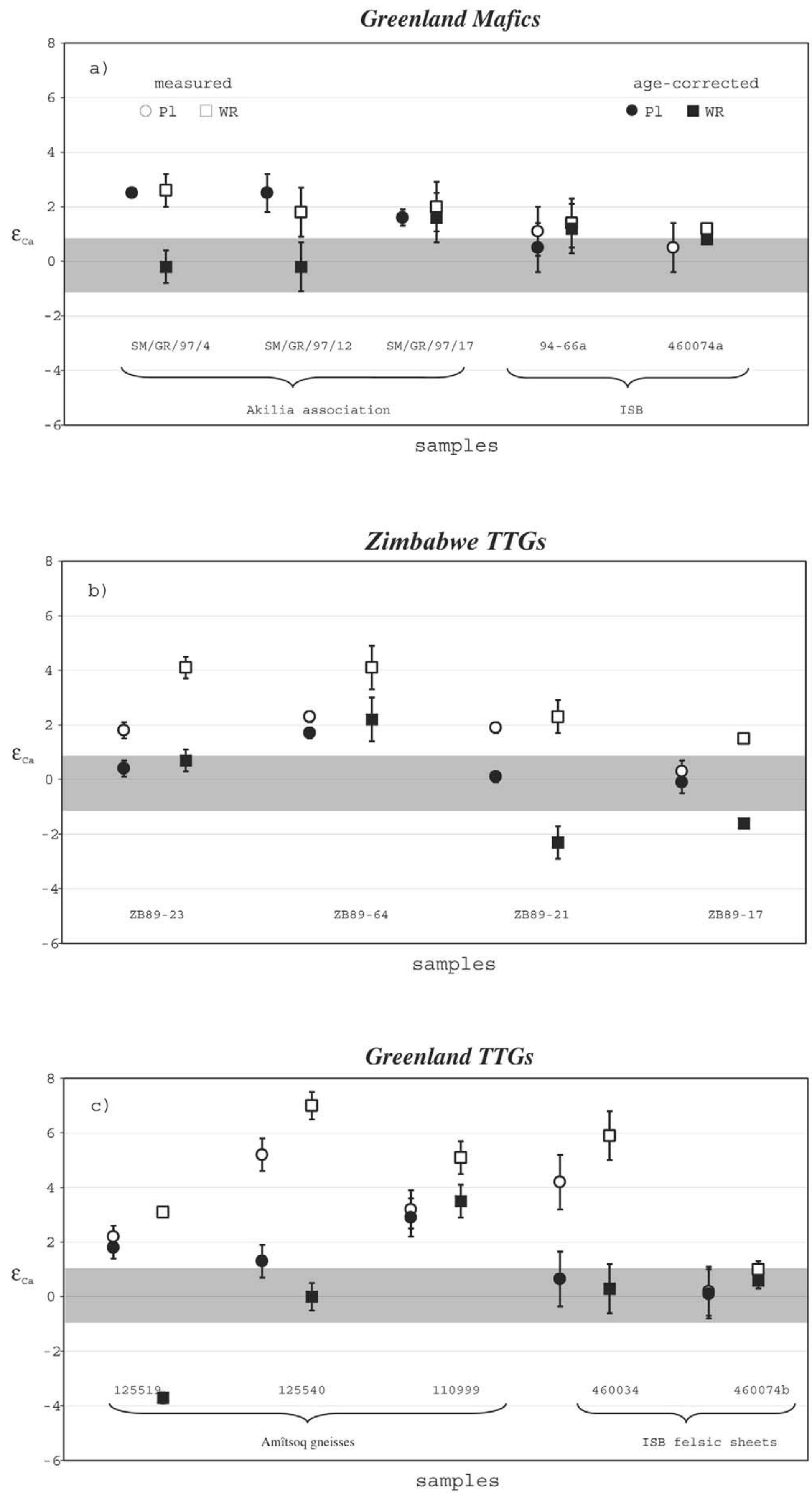


Fig. 4. Figures show a comparison of measured ε_{Ca} values (grey) and back-corrected ratios (black). Corresponding whole rocks (squares) and plagioclase separates (circles) of a sample are grouped and labelled. Error bars represent 2σ errors (Tab.1) and the shaded area the 2σ external reproducibility of $1\varepsilon_{Ca}$ around our measured mantle value. For discussion see text.

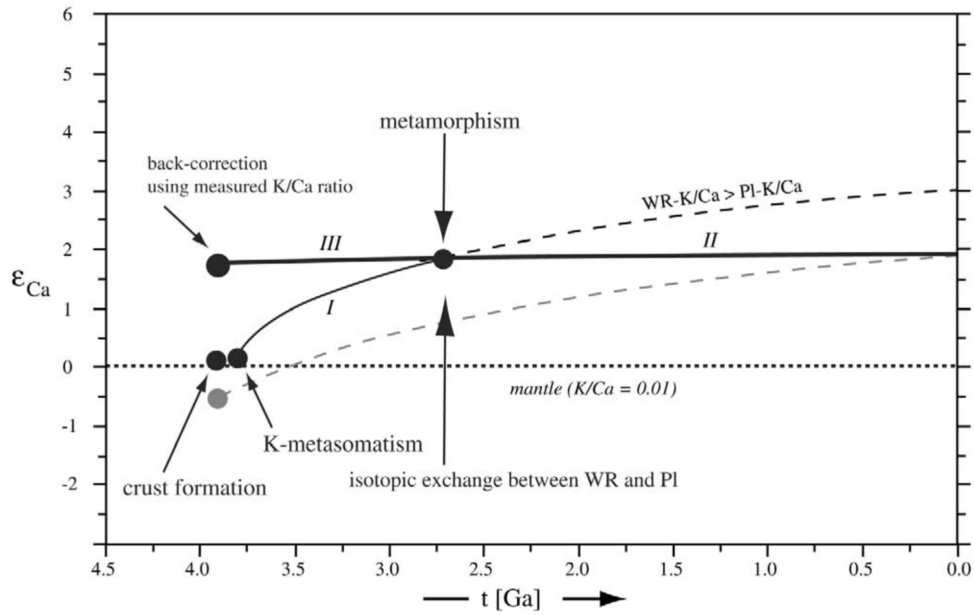


Fig. 5. Schematic ε_{Ca} vs. time diagrams illustrating the effect of metamorphism and/or metasomatism to the age-corrected ε_{Ca} values. Basaltic crust formed at 3.7 Ga underwent K-metasomatism at 3.6 Ga. It evolves with enriched K/Ca along line I. During a high-grade metamorphic event the rock loses K (biotite dehydration) and plagioclase inherits the evolved Ca isotopic composition of the whole rock (isotopic exchange). Age-correction using measured low K/Ca will lead to initial values, which are too high (line III). Recent K-gain can yield a variety of age-corrected initials including meaningless negative values.

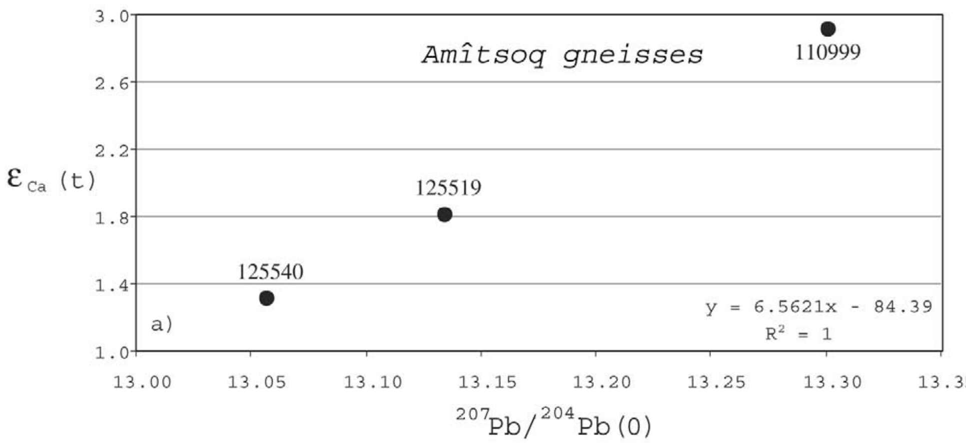
genic signature in both whole rock and plagioclase (e.g., SM/GR/97/17, Fig. 4). This scenario is sketched in Figure 5. In addition, the rocks on Akilia island and the surrounding area were subjected to two younger thermal events, one episode during the intrusion of the nearby Qôrqut granite around 2.55 Ga (Baadsgaard, 1976; Brown et al., 1981; Moorbath et al., 1981) and another between 1.7 and 1.6 Ga during which the biotites lost significant amounts of radiogenic Sr (Pankhurst et al., 1973b). It is probable that the rocks also lost radiogenic Ca together with Sr. This process helps to explain why the whole rock Ca isotopic compositions of samples SM/GR/97/4 and SM/GR/97/12 are not more radiogenic than the plagioclases (Fig. 4a).

As is clearly evident from the mafic samples of the Akilia association, elevated ε_{Ca} from low K/Ca plagioclase is thus not necessarily indicative of prior crustal history but may reflect secondary metamorphic and/or metasomatic disturbance. We now further consider the Archaean TTG gneiss suites studied, in which the role of a prior crustal history is possible but from the analysis above, not required.

5.2. Vestiges of Hadean Crust?

The Zimbabwean case is relatively straight-forward. All but one Zimbabwe TTG are characterised by mantle-like initial ε_{Ca}, which can be readily explained as the signature of juvenile crustal material, extracted from the mantle at a similar time or only shortly before its recorded crustal age (Fig. 2, 4b). Interestingly, some of the samples with mantle like plagioclase ε_{Ca} yield negative values of whole rock $\varepsilon_{Ca}(t)$. This clearly points to an over-correction in the whole rock because during crustal formation K is strongly fractionated from Ca, such that crustal K/Ca ratios are invariably higher than the mantle (Fig. 5). Thus crustal ε_{Ca} values cannot be less radiogenic than the mantle and the negative $\varepsilon_{Ca}(t)$ for the Zimbabwe samples thus points to the effects of other processes. A likely process is recent K gain. The anomalously radiogenic $\varepsilon_{Ca}(t)$ plagioclase of sample (ZB89-64) could reflect incorporation of pre-existing crust into this sample. Yet the systematics are similar to those of the gabbro sample (SM/GR/97/17), in which the radiogenic plagioclase is explained as an open system signature. Ca isotope equilibration between whole rock and plagioclase in a later metamorphic event (also ~2.7 Ga in Zimbabwe) can impart the early isotopic evolution of a high K/Ca TTG to the low K/Ca plagioclase. In the case of this TTG (ZB89-64) the whole rock continued to evolve its ^{40}Ca after metamorphism, in contrast to the mafic Akilia enclave samples, which apparently lost the radiogenic $^{40}Ca/^{44}Ca$ from their biotites (Fig. 5) in a subsequent metamorphic event.

The radiogenic plagioclases ($\varepsilon_{Ca}(t)$ up to 3) from the Greenland TTG gneisses potentially implicate contributions from pre-existing, Hadean crust. However, it is difficult to distinguish such a primary signature from a metamorphic overprint as discussed above. Greenland shows some of the oldest rocks on Earth and is the only documented location of ^{142}Nd anomalies (Harper and Jacobsen, 1992; Boyet et al., 2003; Caro et al., 2003a, 2003b, 2004; Sharma, 2003; Sharma and Chen, 2004). These factors point to an ancient protolith and might suggest some of the high initial Ca reflect incorporation of ancient material in some samples. Yet in the Greenland mafics and Zimbabwe TTG gneisses, it has been highlighted how such signatures may reflect secondary metamorphic events in sam-



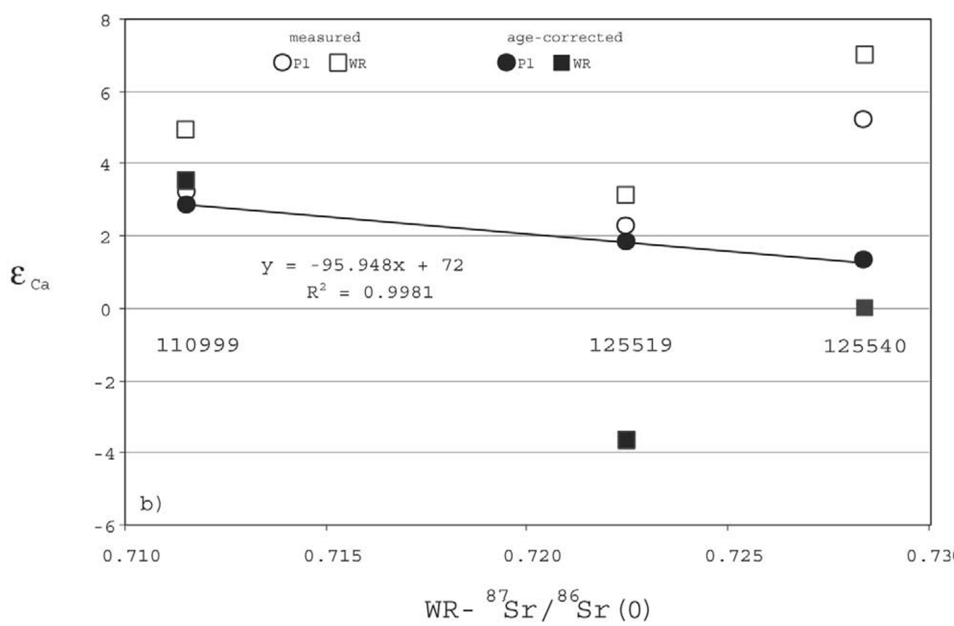


Fig. 6. a: Measured $^{207}Pb/^{204}Pb$ (Kamber and Moorbath, 1998) vs. age-corrected ε_{Ca} values of feldspar separates from the three coastal Amîtsoq gneisses. For discussion see text. 6b: Measured (open symbols) and age-corrected (filled symbols) Ca isotope data of plagioclase separates (circles) and whole rock (squares) are plotted vs. the measured $^{87}Sr/^{86}Sr$ of the whole rock (Moorbath et al., 1972) from the three coastal Amîtsoq gneisses. For discussion see text.

ples that show comparable K-Ca systematics to the Greenland TTG gneisses. It is also significant that the two felsic sheets from the ISB have initial ε_{Ca} within error of the mantle. Thus at least some of the Greenland crust is juvenile.

To help assess if any of the radiogenic initial $^{40}Ca/^{44}Ca$ ratios in the coastal Amîtsoq gneisses, represent the contribution of a long-lived crustal protolith we can examine the systematics of other isotope systems. ^{235}U decays even faster to ^{207}Pb than ^{40}K to ^{40}Ca and so also results in a strong non-linear growth of ^{207}Pb. Therefore, a comparison of Ca and Pb isotope data, $^{207}Pb/^{204}Pb$ in particular, should be interesting. Kamber and Moorbath (1998) published Pb-isotope data on whole rock and feldspar separates from over fifty TTGs from the Itsaq Gneiss Complex in Greenland, including the three Amîtsoq TTG gneisses analysed in this study. Notably measured $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ and age-corrected ε_{Ca} of the feldspars yield good positive correlations ($r^2 = 1.000$, 0.998 and 0.948) albeit on a small data set (Fig. 6a). Since feldspars have both low K/Ca and U/Pb, a metamorphic overprint should make both Pb and Ca isotope ratios more radiogenic. Hence, the correlation in Figure 6a may be interpreted as a result of different amounts of metamorphic resetting. The isotope ratios of the least radiogenic sample, 125540, should most closely approach primary values. Indeed, the feldspar separate of sample 125540 contains some of the least radiogenic terrestrial silicate Pb ever reported and plots close to the Pb mantle evolution curve of Kramers and Tolstikhin (1997) at 3.66 Ga. Ion-microprobe U-Th-Pb data of zircons from this sample are relatively straight-forward, with no evidence for inherited cores and give an age of 3.65Ga (Whitehouse et al., 1999), consistent with the Pb model age. Therefore, the Pb and by inference Ca isotope ratios of the feldspars of this sample appear negligibly disturbed. Its slightly radiogenic Ca isotopic composition, ε_{Ca} = 1.3 thus hints at a contribution of pre-existing crust in this sample.

The most radiogenic sample in Pb and Ca is sample 110999, first cited by Kinny (1986) to contain zircons older than 3.8 Ga. Indeed cathodoluminescence imaging reveals highly complex zircon crystallisation history showing 3.8 Ga old cores and 3.67 Ga old inner rims, both interpreted as being magmatic. Two kinds of metamorphic rims are also recognised, one dated at ≥3.74 Ga and the other between 2.6 and 2.7 Ga (Whitehouse et al., 1999). Such evidence of later disturbance provides further support for our interpretation of highly radiogenic $^{40}Ca/^{44}Ca$ as result of plagioclase recrystallisation and inheritance of radiogenic $^{40}Ca/^{44}Ca$. The high temperature metamorphic event at around 2.7 Ga must have caused also K loss of the whole rock, presumably by mica dehydration, to explain the highly radiogenic age-correct whole rock ε_{Ca}.

The Rb/Sr isotope system is chemically very similar to K/Ca. Therefore, it is perhaps surprising that there is a strong *negative* correlation (r^2 = 0.998) between measured $^{87}Sr/^{86}Sr$ (largely a function of the whole rock Rb/Sr) of the three coastal Amîtsoq gneisses (Moorbath et al., 1972) and the age-corrected ε_{Ca} of the plagioclase separates (Fig. 6b), but no correlations between measured whole rock $^{87}Sr/^{86}Sr$ and whole rock $\varepsilon_{Ca}(0)$ nor plagioclase $\varepsilon_{Ca}(0)$. However, the isotope systems differ significantly in that the half-life of ^{87}Rb is much longer than ^{40}K. Hence, K and Rb gain in the latter half of Earth history will have little effect on the Ca isotopic composition but can strongly increase the $^{87}Sr/^{86}Sr$. The reverse is true for the early Archaean. Several episodes of K and Rb gain and loss can thus lead to an apparent decoupling of the isotope ratios without real chemical separation of the two pairs K-Rb and Ca-Sr. Sample 125540 has the lowest $\varepsilon_{Ca}(t)$ of the plagioclase but the highest measured $^{87}Sr/^{86}Sr$ of the whole rock (unfortunately no plagioclase $^{87}Sr/^{86}Sr$ data are available). As discussed above, the Pb isotope data for this sample indicate no metamorphism. Therefore the rock maintained high K/Ca and Rb/Sr ratios though time, which evolved to high present day $^{40}Ca/^{44}Ca$ and $^{87}Sr/^{86}Sr$. Yet the plagioclase remained close to closed system and preserved the initial Ca (and probably Sr) isotopic composition of its source. Sample 110999 on the other hand, is strongly influenced by high temperature metamorphic overprint (see above) causing plagioclase recrystallisation and biotite dehydration. Therefore, the rock lost K and Rb yielding the least radiogenic Sr isotopic composition but the plagioclases reveal the inherited radiogenic ε_{Ca}. Sample 125519 has also experienced Ca isotope resetting and K-Rb loss due to its high $\varepsilon_{Ca}(t)$ of 1.8. Besides, it has been clearly gained K and probably Rb because the whole rock is widely over-corrected ($\varepsilon_{Ca}(t)$ = −3.7). This gain must have happened during the Proterozoic to allow substantial ^{87}Sr ingrowth but little effect on the $^{40}Ca/^{44}Ca$.

The empiric identification of Ca isotopic resetting of plagioclase is disappointing in the context of the original aim of this study. The apparent complete resetting of the Ca isotopic system in plagioclase, despite very low diffusion coefficients, however, highlights the difficulty of interpreting original signatures in Archaean rocks. Nevertheless, this study shows that in both Greenland and Zimbabwe there are TTG gneisses that clearly have juvenile initial ε_{Ca}. Samples with mantle signatures are well defined in the Ca system, given the lack of age correction required in most plagioclases and the negligibly evolving mantle baseline. Interpretation of elevated $^{40}Ca/^{44}Ca$ transpires to be problematic due to the potential effects of metamorphic disturbance. Thus an important potential use of the Ca system is to identify juvenile crustal samples that clearly remained undisturbed by subsequent processes. This is a significant independent constraint in interpreting other radiogenic isotope signatures. Notably for the generally little disturbed Zimbabwe samples initial $\varepsilon_{Nd}(t)$ are ~0.8 (Moorbath et al., 1986). The supplementary Ca isotope data suggests this a likely and reliable estimate for the mantle Nd isotopic composition of the time and is in good agreement with findings of Nägler and Kramers (1998). The complexity of the Ca isotopic systematics of some Greenland samples, however, underscores the difficulty in interpreting mantle ε_{Nd} from this locality (Bennett et al., 1993; Gruau et al., 1996; Moorbath et al., 1997; Bennett and Nutman, 1998; Kamber et al., 1998; Frei et al., 2002).

6. CONCLUSIONS

Ca isotope ratios have the potential to distinguish between end member scenarios of crustal evolution. Unradiogenic mantle-like ε_{Ca} values from Zimbabwe TTG leaves the 'steady state' model of continental growth (Armstrong, 1968) unsupported, which would predict the presence of contributions of Hadean crust in all Archaean cratons.

This study highlights that despite low Ca diffusion coefficients in low K/Ca plagioclase, initial Ca isotopic ratios can be perturbed to significantly radiogenic values by subsequent high temperature metamorphism. This complicates the application of radiogenic Ca isotope measurements in determining early continental growth. In conjunction with Pb and Sr isotope data, however, the results indicate that some felsic crust in Greenland reflects a Hadean prehistory with a source composition $\varepsilon_{Ca}(3.65)$ around 1. In contrast, felsic sheets from the Isua supracrustal belt represent juvenile crust.

Early Archaean TTG (~3.6 Ga) from Zimbabwe dominantly show initial ε_{Ca} in plagioclases within error of the mantle, which is well defined in the K-Ca system. Thus these samples appear to have been little disturbed by major subsequent metamorphism. Consequently the initial ε_{Nd} of these samples of around 0.8 should provide a reliable record of mantle isotopic values at this time.

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REFERENCES

Albarède F., Blichert-Toft J., Vervoort J. D., Gleason J. D., and Rosing M. (2000) Hf-Nd evidence for a transient dynamic regime in the early terrestrial mantle. *Nature* **404,** 488–490.

Amelin Y., Lee D. C., Halliday A. N., and Pidgeon R. T. (1999) Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons. *Nature* **399,** 252–255.

Amelin Y., Lee D. C., and Halliday A. N. (2000) Early-middle Archaean crustal evolution deduced from Lu-Hf and U-Pb isotopic studies of single zircon grains. *Geochim. Cosmochim. Acta* **64,** 4205–4226.

Armstrong R. L. (1968) A model for Sr and Pb isotope evolution in a dynamic Earth. *Rev. Geophys.* **6,** 175–199.

Armstrong R. L. (1981) Radiogenic isotopes; the case for crustal recycling on a near-steady-state no-continental-growth Earth. *Philosophical Transaction of the Royal Society of London, Series A: Mathematical and Physical Sciences* **301,** 443–472.

Baadsgaard H. (1973) U-Th-Pb dates on zircons from the early Precambrian Amîtsoq gneisses, Godthåb district, West Greenland. *Earth Planet. Sci. Lett.* **19,** 22–28.

Baadsgaard H. (1976) Further U-Th-Pb dates on zircons from the early Precambrian rocks of the Godthåbsfjord area, West Greenland. *Earth Planet. Sci. Lett.* **33,** 261–267.

Baadsgaard H., Nutman A. P., Rosing M., Bridgwater D., and Longstaffe F. J. (1986a) Alteration and metamorphism of Amîtsoq gneisses from the Isukasia area, West Greenland: Recommendations for isotope studies of the early crust. *Geochim. Cosmochim. Acta* **50,** 2165–2172.

Baadsgaard H., Nutman A. P., and Bridgwater D. (1986b) Geochronology and isotope variation of the early Archaean Amîtsoq gneisses of the Isukasia area, southern West Greenland. *Geochim. Cosmochim. Acta* **50,** 2173–2183.

Bennett V. C. and Nutman A. P. (1998) Extreme Nd isotope heterogeneity in the early Archean—fact or fiction? Case histories from northern Canada and West Greenland—Comment. *Chem. Geol.* **148,** 213–317.

Bennett V. C., Nutman A. P., and McCulloch M. T. (1993) Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet. Sci. Lett.* **119,** 299–317.

Black L. P., Gale N. H., Moorbath S., Pankhurst R. J., and McGregor V. R. (1971) Isotopic dating of very early Precambrian amphibolite facies gneisses from the Godthåb district, West Greenland. *Earth Planet. Sci. Lett.* **12,** 245–259.

Blichert-Toft J., Albarède F., Rosing M., Frei R., and Bridgwater D. (1999) The Nd and Hf isotope evolution of the mantle through the Archean. Results from the Isua supracrustals, West Greenland and from the Birimian terranes of West Africa. *Geochim. Cosmochim. Acta* **63,** 3901–3914.

Bizzarro M., Baker J. A., Haack H., Ulfbeck D., and Rosing M. (2003) Early history of Earth's crust-mantle system inferred from hafnium isotopes in chondrites. *Nature* **421,** 931–933.

Boyet M., Blichert-Toft J., Rosing M., Storey M., Télouk P., and Albarède F. (2003) ^{142}Nd evidence for early Earth differentiation. *Earth Planet. Sci. Lett.* **214,** 427–442.

Bowring S. A. and Housh T. B. (1995) The earth's early evolution. *Science* **269,** 1535–1540.

Bowring S. A. and Williams I. S. (1999) Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. *Contrib. Mineral. Petrol.* **134,** 3–16.

Bowring S. A., King J. E., Housh T. B., Isachsen C. E., and Podosek F. A. (1989) Neodymium and lead isotope evidence for enriched early Archean crust in North America. *Nature* **340,** 222–225.

Brown M., Friend C. R. L., McGregor V. R., and Perkins W. T. (1981) The late Archaean Qôrqut granite complex of southern West Greenland. *J. Geophys. Res.* **86,** 10617–10632.

Cherniak D. J. and Watson E. B. (1994) A study of strontium diffusion in plagioclase using Rutherford backscattering spectroscopy. *Geochim. Cosmochim. Acta* **58,** 5179–5190.

Caro G., Bourdon B., Birck J.-L., and Moorbath S. (2003a) ^{146}Sm/^{142}Nd precise evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. *Nature* **423,** 428–432.

Caro G., Bourdon B., Birck J.-L., and Moorbath S. (2003b) ^{142}Nd isotope constraints on the evolution of the Hadean Earth. *Geochim. Cosmochim. Acta* **67,** Suppl. 1, A53.

Caro G., Bourdon B., Birck J.-L., and Moorbath S. (2004) ^{146}Sm-^{142}Nd constraints on the evolution of the Hadean mantle. *Geochim. Cosmochim. Acta* **68,** Suppl. 1, A746.

Fedo C. M. and Whitehouse M. J. (2002) Metasomatic origin of Quartz-Pyroxene rock, Akilia, Greenland and implication for Earth's earliest life. *Science* **296,** 1448–1452.

Fletcher I. R., Maggi A. L., Rosman K. J. R., and McNaughton N. J. (1997a) Isotopic abundance measurements of K-Ca using a wide-dispersion multi-collector mass spectrometer and low-fractionation ionisation techniques. *Int. J. Mass Spectrom. Ion Proc.* **163,** 1–17.

Fletcher I. R., McNaughton N. J., Pidgeon R. T., and Rosman K. J. R. (1997b) Sequential closure of K-Ca and Rb-Sr isotopic systems in Archaean micas. *Chem. Geol.* **138,** 289–301.

Frei R. and Jensen B. K. (2003) Re-Os, Sm-Nd isotope- and REE systematics on ultramafic rocks and pillow basalts from the Earth's oldest oceanic crustal fragments (Isua Supracrustal Belt and Ujaragssuit nunât area, W Greenland). *Chem. Geol.* **196,** 163–191.

Frei R., Bridgwater D., Rosing M., and Stecher O. (1999) Controversial Pb-Pb and Sm-Nd isotope results in the early Archean Isua (West Greenland) oxide iron formation: Preservation of primary signatures versus secondary disturbances. *Geochim. Cosmochim. Acta* **63,** 473–488.

Frei R., Rosing M. T., Waight T. E., and Ulfbeck D. G. (2002) Hydrothermal-metasomatic and tectono-metamorphic processes in the Isua supracrustal belt (West Greenland): A multi-isotopic investigation of their effects on the Earth's oldest oceanic crustal sequence. *Geochim. Cosmochim. Acta* **66,** 467–486.

Frei R., Polat A., and Meibom A. (2004) The Hadean upper mantle conundrum: Evidence for source depletion and enrichment from Sm-Nd, Re-Os and Pb isotopic compositions in 3.71 Gy boninite-like metabasalts from the Isua Supracrustal Belt, Greenland. *Geochim. Cosmochim. Acta* **68,** 1645–1660.

Giletti B. J. and Casserly J. E. D. (1994) Strontium diffusion kinetics in plagioclase feldspars. *Geochim. Cosmochim. Acta* **58,** 3785–3793.

Griffin W. L., McGregor V. R., Nutman A., Taylor P. N., and Bridgwater D. (1980) Early Archean metamorphism south of Ameralik, West Greenland. *Earth Planet. Sci. Lett.* **50,** 59–74.

Gruau G., Rosing M., Bridgwater D., and Gill R. C. O. (1996) Metamorphism and Sm-Nd remobilization in the >3.7 Ga Isua supracrustal belt of West Greenland: implications for isotope models of early Earth differentiation. *Chem. Geol.* **133,** 225–240.

Harper C. L. and Jacobsen S. B. (1992) Evidence from coupled ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd systematics for very early (4.5-Gyr) differentiation of the Earth's mantle. *Nature* **360,** 728–732.

Hart S. R. and Zindler A. (1986) In search of a bulk-Earth composition. *Chem. Geol.* **57,** 247–267.

Hart S. R. and Zindler A. (1989) Isotope fractionation laws: a test using calcium. *Int. J. Mass Spectrom. Ion Proc.* **89,** 287–301.

Hawkesworth C. J., Moorbath S., and O'Nions R. K. (1975) Age relationships between greenstone belts and "granites" in the Rhodesian Archean Craton. *Earth Planet. Sci. Lett.* **25,** 251–262.

Hickman M. H. (1978) Isotopic evidence for crustal reworking in the Rhodesian Archean craton, southern Africa. *Geol.* **6,** 214–216.

Hurley P. M. and Rand J. R. (1969) Pre-drift continental nuclei. *Science* **164,** 1229–1242.

Kamber B. S. and Moorbath S. (1998) Initial Pb of the Amîtsoq gneiss revisited: implication for the timing of early Archaean crustal evolution in West Greenland. *Chem. Geol.* **150,** 19–41.

Kamber B. S., Moorbath S., and Whitehouse M. J. (1998) Extreme Nd isotope heterogeneity in the early Archean—fact or fiction? Case histories from northern Canada and West Greenland—Reply. *Chem. Geol.* **148,** 219–224.

Kinny P. D. (1986) 3820 Ma zircons from a tonalitic Amîtsoq gneiss in the Godthåb district of southern West Greenland. *Earth Planet. Sci. Lett.* **79,** 337–347.

Luais B. and Hawkesworth C. J. (1994) The generation of continental crust: An integrated study of crust-forming processes in the Archean of Zimbabwe. *J. Petrol.* **35,** 43–93.

Marshall B. D. and DePaolo D. J. (1982) Precise age determinations and petrogenetic studies using the K-Ca method. *Geochim. Cosmochim. Acta* **46,** 2537–2545.

Marshall B. D. and DePaolo D. J. (1989) Ca isotopes in igneous rocks and the origin of granite. *Geochim. Cosmochim. Acta* **53,** 917–922.

McGregor V. R. and Mason B. (1977) Petrogenesis and geochemistry of metabasaltic and metasedimetary enclaves in the Amîtsoq gneisses, West Greenland. *Am. Mineral.* **62,** 887–904.

Moorbath S., O'Nions R. K., Pankhurst R. J., Gale N. H., and McGregor V. R. (1972) Further Rubidium-Strontium age determinations on the very early Precambrian rocks of the Godthaab district, West Greenland. *Nature* **240,** 78–82.

Moorbath S., O'Nions R. K., and Pankhurst R. J. (1973) Early Archaean age for the Isua Iron Formation, West Greenland. *Nature* **245,** 138–139.

Moorbath S., O'Nions R. K., and Pankhurst R. J. (1975) The evolution of early Precambrian crustal rocks at Isua, West Greenland—geochemical and isotopic evidence. *Earth Planet. Sci. Lett.* **27,** 229–239.

Moorbath S., Wilson J. F., and Cotterill P. (1976) Early Archean age for the Sebakwean Group at Selukwe, Rhodesia. *Nature* **264,** 536–538.

Moorbath S., Allaart J. H., Bridgwater D., and McGregor V. R. (1977a) Rb-Sr ages of early Archean supracrustal rocks and Amîtsoq gneisses at Isua. *Nature* **270,** 43–45.

Moorbath S., Wilson J. F., Goodwin R., and Humm M. (1977b) Further Rb-Sr age and isotope data on early and late Archean rocks from the Rhodesian craton. *Precamb. Res.* **5,** 229–239.

Moorbath S., Taylor P. N., and Goodwin R. (1981) Origin of granitic magma by crustal remobilisation: Rb-Sr and Pb/Pb geochronology and isotopic geochemistry of the late Archaean Qôrqut granite complex of southern West Greenland. *Geochim. Cosmochim. Acta* **45,** 1051–1060.

Moorbath S., Taylor P. N., and Jones N. W. (1986) Dating the oldest terrestrial rocks-fact and fiction. *Chem. Geol.* **57,** 63–86.

Moorbath S., Whitehouse M. J., and Kamber B. S. (1997) Extreme Nd isotope heterogeneity in the early Archean—fact or fiction? Case histories from northern Canada and West Greenland. *Chem. Geol.* **135,** 213–231.

Myers J. S. and Crowley J. L. (2000) Vestiges on life in the oldest Greenland rocks? A review of early Archean geology in the Godthåbsfjord region and reappraisal of field evidence for >3850 Ma life on Akilia. *Precamb. Res.* **103,** 101–124.

Nägler T. N. and Kramers J. D. (1998) Nd isotopic evolution of the upper mantle during the Precambrian: models, data and the uncertainty of both. *Precamb. Res.* **91,** 233–252.

Nägler T. N. and Villa I. M. (2000) In pursuit of the ^{40}K branching ratios: K-Ca and ^{39}Ar-^{40}Ar dating of gem silicates. *Chem. Geol.* **169,** 5–16.

Nelson D. R. and McCulloch M. T. (1989) Petrogenetic applications of the ^{40}K-^{40}Ca radiogenic decay scheme—a reconnaissance study. *Chem. Geol.* **79,** 257–293.

Niu Y. L., Collerson K. D., Batiza R., Wendt J. I., and Regelous M. (1999) Origin of enriched-type mid-ocean ridge basalt at ridges far from mantle plumes: The East Pacific Rise at 11°20′N. *J. Geophys. Res. Solid Earth* **104,** 7067–7087.

Nutman A. P., McGregor V. R., Friend C. R. L., Bennett V. C., and Kinny P. D. (1996) The Itsaq Gneiss Complex of southern West Greenland; the world's most extensive record of early crustal evolution (3900–3600 Ma). *Precamb. Res.* **78,** 1–39.

Nutman A. P., Mojzsis S. J., and Friend C. R. L. (1997a) Recognition of ≥3850 Ma water-lain sediments in West Greenland and their significance for the early Archaean Earth. *Geochim. Cosmochim. Acta* **61,** 2475–2484.

Nutman A. P., Bennett V. C., Friend C. R. L., and Rosing M. T. (1997b) ~3710 and ≥3790 Ma volcanic sequences in the Isua (Greenland) supracrustal belt; structural and Nd isotope implications. *Chem. Geol.* **141,** 271–287.

Nutman A. P., Bennett V. C., Friend C. R. L., and Norman M. D. (1999) Meta-igneous (non-gneissic) tonalites and quartz-diorites from an extensive ca. 3800 Ma terrain south of the Isua supracrustal belt, southern West Greenland: Constraints on early crust formation. *Contrib. Mineral. Petrol.* **137,** 364–388.

Pankhurst R. J., Moorbath S., Rex D. C., and Turner G. (1973a) Mineral age patterns in ca. 3700 My old rocks from West Greenland. *Earth Planet. Sci. Lett.* **20,** 157–170.

Pankhurst R. J., Moorbath S., and McGregor V. R. (1973b) Late event in the geological evolution of the Godthåb district, West Greenland. *Nature* **243,** 24–26.

Rose N. M., Rosing M. T., and Bridgwater D. (1996) The origin of metacarbonate rocks in the Archaean Isua supracrustal belt, West Greenland. *Am. J. Sci.* **296,** 1004–1044.

Rosing M. T., Rose N. M., Bridgwater D., and Thomsen H. S. (1996) Earliest part of Earth's stratigraphic record: a reappraisal of the >3.7 Ga Isua (Greenland) supracrustal sequence. *Geol.* **24,** 43–46.

Rudnick R. L. and Fountain D. M. (1995) Nature and composition of the continental crust: a lower crustal perspective. *Rev. Geophys.* **33,** 267–309.

Russell W. A., Papanastassiou D. A., and Tombrello T. A. (1978) Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* **42,** 1075–1090.

Scherer E., Münker C., and Mezger K. (2001) Calibration of the Lu-Hf clock. *Science* **293,** 683–687.

Schiøtte L. and Compston W. (1990) U-Pb age pattern for single zircon from the early Archaean Akilia association south of Ameralik fjord, southern West Greenland. *Chem. Geol.* **80,** 147–157.

Sharma M. (2003) Correlation between ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd and the issue of ^{142}Nd anomalies in early Archean rocks. *Geochim. Cosmochim. Acta* **67,** Suppl. 1, A425.

Sharma M. and Chen C. (2004) Early Earth differentiation using coupled ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd. *Geochim. Cosmochim. Acta* **68,** Suppl. 1, A746.

Shih C.-Y., Nyquist L. E., and Wiesmann H. (1993) K-Ca chronology of lunar granites. *Geochim. Cosmochim. Acta* **57,** 4827–4841.

Shih C.-Y., Nyquist L. E., Bogard D. D., and Wiesmann H. (1994) K-Ca and Rb-Sr dating of two lunar granites: Relative chronometer resetting. *Geochim. Cosmochim. Acta* **58,** 3101–3116.

Steiger R. H. and Jäger E. (1977) Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* **115,** 197–209.

Taylor P. N., Jones N. W., and Moorbath S. (1984) Isotopic assessment of relative contributions from crust and mantle sources to the magma genesis of Precambrian granitoid rocks. *Philosophical Transaction of the Royal Society of London, Series A: Mathematical and Physical Sciences* **310,** 605–625.

Taylor P. N., Kramers J. D., Moorbath S., Wilson J. F., Orpen J. L., and Martin A. (1991) Pb/Pb, Sm-Nd and Rb-Sr geochronology in the Archean Craton of Zimbabwe. *Chem. Geol. (Iso. Sect.)* **87,** 175–196.

Taylor S. R. and McLennan S. M. (1985) The Continental Crust: Its composition and evolution. Blackwell Scientific Boston, Mass., 312 pp.

Thompson M., Potts P. J., Kane J. S., and Chappell B. W. (1999) GeoPT3. International proficiency test for analytical geochemistry laboratories—report on Round 3. *Geostand. News.* **23,** 87–121.

Whitehouse M. J. and Kamber B. S. (2002) On the overabundance of light rare earth elements in terrestrial zircons and its implication for Earth's earliest magmatic differentiation. *Earth Planet. Sci. Lett.* **204,** 333–346.

Whitehouse M. J. and Kamber B. S. (2003) A rare earth element study of complex zircons from early Archaean Amîtsoq gneisses, Godthåbsfjord, south-west Greenland. *Precamb. Res.* **126,** 363–377.

Whitehouse M. J., Kamber B. S., and Moorbath S. (1999) Age significance of U-Th-Pb zircon data from early Archean rocks of west Greenland—a reassessment based on combined ion-microprobe and imaging studies. *Chem. Geol.* **160,** 201–224.

Wilde S. A., Valley J. W., Peck W. H., and Graham C. M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409,** 175–178.

Villa I. M., Kamber B. S., and Nägler T. F. (2001) The Nd and Hf isotopic evolution of the mantle through the Archean. Results from the Isua supracrustals, West Greenland and from the Birimian terranes of West Africa—comment. *Geochim. Cosmochim. Acta* **65,** 2017–2021.